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## USE OF POLYMERS FOR STARCH MODIFICATION

The invention relates to the use of polymers for starch modification, the polymers being used in the form of  
5 their polymer powders or as an aqueous polymer dispersion.

Starch is frequently used for the production of biodegradable moldings. Starch, in particular  
10 destructured starch, is however generally hard and brittle in the dried state and cannot be molded at relatively high temperatures. As a result of adding water, the internal bonds are broken and the material becomes softer and moldable. This moldability can be  
15 increased by adding thermoplastic polymers in order to obtain an extrudable or injection moldable material. Frequently, the starch with residual moisture is pretreated (destructured) and pelleted in a separate step. These pellets, together with polymer granules,  
20 are then brought into the desired form thermomechanically.

EP-A 327505 discloses the mixing of granular, destructured starch and granular, water-insoluble  
25 thermoplastics, and the processing of the melt of this mixture to give moldings.

WO-A 99/29733 describes a process in which potato peelings and potato residues are molded together with  
30 biodegradable polymers and plasticizers by thermomechanical treatment to give bodies having good mechanical strength and biodegradability.

EP-A 611804 relates to extrudable starch compositions  
35 comprising thermoplastic polyvinyl alcohol, thermoplastically modified starch, in particular hydroxypropylated starch, and plasticizers.

EP-A 522358 describes thermoplastically processible materials comprising starch and extremely high molecular weight acrylate polymers, which materials give readily moldable, strong moldings.

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EP-A 1229075 describes a thermoplastic polymer composite based on natural starch, a synthetic polymer, a compatibilizer, a destructuring agent and a sheet silicate.

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It was the object to provide thermoplastically modified starch compositions which, in addition to very good processibility, also lead to moldings which are distinguished by high strength, in particular in the wet state.

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The invention relates to the use of polymers, in the form of their polymer powders or as an aqueous polymer dispersion, for starch modification, characterized in that polymers stabilized with a protective colloid and/or emulsifier and comprising one or more comonomer units from the group consisting of vinyl esters of straight-chain or branched alkylcarboxylic acids having 1 to 18 carbon atoms, acrylates or methacrylates of branched or straight-chain alcohols having 1 to 15 carbon atoms, dienes, olefins, vinylaromatics and vinyl halides are used, which polymers optionally also contain from 0.1 to 20.0% by weight of functional comonomer units from the group consisting of carboxyl-, hydroxyl-, epoxy- and NH-functional, ethylenically unsaturated comonomers, the data in % by weight being based on the total weight of the polymer.

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Suitable vinyl esters are vinyl esters of straight-chain or branched carboxylic acids having 1 to 18 carbon atoms. Preferred vinyl esters are vinyl acetate, vinyl propionate, vinyl butyrate, vinyl 2-ethylhexanoate, vinyl laurate, 1-methylvinyl acetate, vinyl pivalate and vinyl esters of  $\alpha$ -branched

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monocarboxylic acids having 5 to 15 carbon atoms, for example VeoVa9<sup>R</sup> or VeoVa10<sup>R</sup> (trade names of Shell). Vinyl acetate is particularly preferred.

5     Suitable monomers from the group consisting of the esters of acrylic acid or methacrylic acid are esters of straight-chain or branched alcohols having 1 to 15 carbon atoms. Preferred methacrylates or acrylates are methyl acrylate, methyl methacrylate, ethyl acrylate,  
10    ethyl methacrylate, propyl acrylate, propyl methacrylate, n-butyl acrylate, n-butyl methacrylate, tert-butyl acrylate, tert-butyl methacrylate 2-ethylhexyl acrylate and norbornyl acrylate. Methyl acrylate, methyl methacrylate, n-butyl acrylate, 2-  
15    ethylhexyl acrylate and norbornyl acrylate are particularly preferred.

Suitable dienes are 1,3-butadiene and isoprene. Examples of copolymerizable olefins are ethene and  
20    propene. Styrene and vinyltoluene can be copolymerized as vinylaromatics. From the group consisting of vinyl halides, vinyl chloride is usually used.

In a preferred embodiment, the polymer also contains  
25    from 0.1 to 20% by weight, based on the total weight of the polymer, of one or more comonomer units from the group consisting of carboxy-functional, hydroxy-functional, epoxy-functional and NH-functional comonomers.

30    Suitable carboxy-functional comonomers are ethylenically unsaturated mono- and dicarboxylic acids having 2 to 10 carbon atoms, preferably acrylic acid, methacrylic acid, crotonic acid, itaconic acid, fumaric  
35    acid and maleic acid. The carboxyl function can also be introduced into the copolymer by copolymerization of maleic anhydride. Suitable hydroxy-functional comonomers are hydroxyalkyl acrylates and hydroxyalkyl methacrylates having a C<sub>1</sub>- to C<sub>8</sub>-alkyl radical,

preferably hydroxyethyl acrylate and methacrylate, hydroxypropyl acrylate and methacrylate, hydroxybutyl acrylate and methacrylate. Suitable epoxy-functional comonomers are glycidyl acrylate and glycidyl methacrylate. Suitable NH-functional comonomers are acrylamide, methacrylamide, N-alkylol-functional comonomers having C<sub>1</sub>- to C<sub>4</sub>-alkylol radical, preferably N-methylol radical, such as N-methylolacrylamide (NMA), N-methylolmethacrylamide, N-methylolallylcarbamate, C<sub>1</sub>- to C<sub>4</sub>-alkyl ethers of N-methylolacrylamide, N-methylolmethacrylamide and N-methylolallylcarbamate, for example their isobutoxy ethers, and C<sub>1</sub>- to C<sub>4</sub>-alkyl esters of N-methylolacrylamide, of N-methylolmethacrylamide and of N-methylolallylcarbamate.

N-Methylol-functional comonomer units are particularly preferred, and N-methylolacrylamide, N-methylolmethacrylamide, N-methylolallylcarbamate, C<sub>1</sub>- to C<sub>4</sub>-alkyl ethers of N-methylolacrylamide, such as the isobutoxy ether, are most preferred. The proportion of functional units is preferably from 0.1 to 10% by weight, based on the total weight of the copolymer.

Preferred polymers are the below-mentioned polymers which optionally also have the abovementioned units containing functional groups, in the amounts described above:

vinyl acetate polymers;  
vinyl ester/ethylene copolymers, such as vinyl acetate/ethylene copolymers;  
vinyl ester/ethylene/vinyl chloride copolymers, vinyl acetate and/or vinyl propionate and/or one or more copolymerizable vinyl esters, such as vinyl laurate, vinyl pivalate, vinyl 2-ethylhexanoate, vinyl esters of an alpha-branched carboxylic acid having 5 to 15 carbon atoms, in particular vinyl versatate (Veova9<sup>R</sup>, Veova10<sup>R</sup>), preferably being contained as vinyl esters;  
vinyl acetate copolymers comprising one or more copolymerizable vinyl esters, such as vinyl laurate,

vinyl pivalate, vinyl 2-ethylhexanoate, vinyl esters of an alpha-branched carboxylic acid having 5 to 15 carbon atoms, in particular vinyl versatate (VeoVa9<sup>R</sup>, VeoVa10<sup>R</sup>), which optionally also contain ethylene;

5. vinyl ester/acrylate copolymers, in particular comprising vinyl acetate and butyl acrylate and/or 2-ethylhexyl acrylate, which optionally also contain ethylene;

10 vinyl ester/acrylate copolymers comprising vinyl acetate and/or vinyl laurate and/or vinyl versatate and acrylates, in particular butyl acrylate or 2-ethylhexyl acrylate, which optionally also contain ethylene;

(meth)acrylate and styrene polymers, such as copolymers comprising n-butyl acrylate and/or 2-ethylhexyl  
15 acrylate;

copolymers of methyl methacrylate with butyl acrylate and/or 2-ethylhexyl acrylate, and/or 1,3-butadiene;

styrene/1,3-butadiene copolymers and styrene/(meth)acrylate copolymers, such as styrene/butyl  
20 acrylate, styrene/methyl methacrylate/butyl acrylate or styrene/2-ethylhexyl acrylate, it being possible for the butyl acrylate used to be n-butyl acrylate, isobutyl acrylate and tert-butyl acrylate.

25 Vinyl ester polymers are particularly preferred, in particular vinyl acetate polymers, vinyl acetate/ethylene copolymers, vinyl acetate/ethylene/vinyl chloride copolymers, vinyl ester/acrylate copolymers, in particular comprising vinyl acetate and  
30 butyl acrylate and/or 2-ethylhexyl acrylate. Most preferred are N-methylol-functional vinyl ester polymers, such as vinyl acetate/N-methylolacrylamide copolymers and vinyl acetate/ethylene/ N-methylolacrylamide copolymers.

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The choice of monomers or the choice of the proportions by weight of the comonomers is made in such a way that the polymers have a glass transition temperature T<sub>g</sub> of from -30°C to +120°C, preferably from +10°C to +80°C.

The glass transition temperature  $T_g$  of the polymer can be determined in a known manner by means of differential scanning calorimetry (DSC). The  $T_g$  can also be calculated approximately in advance by means of the Fox equation. According to Fox T.G., Bull. Am. Physics Soc. 1, 3, page 123 (1956), the following is applicable:  $1/T_g = x_1/T_{g1} + x_2/T_{g2} + \dots + x_n/T_{gn}$ , where  $x_n$  is the mass fraction (% by weight/100) of the monomer  $n$  and  $T_{gn}$  is the glass transition temperature in Kelvin of the homopolymer of the monomer  $n$ .  $T_g$  values for homopolymers appear in Polymer Handbook 2nd Edition, J. Wiley & Sons, New York (1975).

The polymers can be prepared by means of known free radical polymerization processes, for example by means of aqueous suspension polymerization or aqueous emulsion polymerization. Emulsion polymerization is preferred. All conventional drying processes may be used for drying the solutions or dispersions: spray drying, roll drying, freeze drying, belt drying, coagulation with subsequent fluidized-bed drying. Spray drying and roll drying processes are preferably used for the preparation of polymer powders redispersible in water. During the drying, additives, such as flameproofing agents, plasticizers, fillers and complexing agents, may optionally be added.

Emulsifier-stabilized polymers contain from 1 to 20% by weight of emulsifier, based on polymer. Suitable emulsifiers are anionic, cationic and nonionic emulsifiers, for example anionic surfactants, such as alkylsulfates having a chain length of from 8 to 18 carbon atoms, alkyl or alkylaryl ether sulfates having 8 to 18 carbon atoms in the hydrophobic radical and up to 40 ethylene oxide or propylene oxide units, alkane- or alkylarylsulfonates having 8 to 18 carbon atoms, esters and monoesters of sulfosuccinic acids with monohydric alcohols or alkylphenols, or nonionic surfactants, such as alkylpolyglycol ethers or

alkylaryl polyglycol ethers having 8 to 40 ethylene oxide units.

5 Polymers stabilized with protective colloid are preferred. Suitable protective colloids are polyvinyl alcohols, polyvinyl acetals, polyvinylpyrrolidones, celluloses and their derivatives, such as carboxymethyl, methyl, hydroxyethyl and hydroxypropyl derivatives, poly(meth)acrylic acid, copolymers of  
10 (meth)acrylates with carboxy-functional comonomer units, poly(meth)acrylamide, polyvinylsulfonic acids and their copolymers, melamineformaldehydesulfonates, naphthaleneformaldehydesulfonates, styrene/maleic acid and vinyl ether/maleic acid copolymers, starch and  
15 dextrans. The proportion of protective colloid is in general from 1 to 30% by weight, based on the weight of the polymer.

20 Partly hydrolyzed polyvinyl alcohols having a degree of hydrolysis of from 80 to 95 mol% and a Höppler viscosity, in 4% strength aqueous solution, of from 1 to 30 mPa·s (method according to Höppler at 20°C, DIN 53015) are preferred. Partly hydrolyzed, hydrophobically modified polyvinyl alcohols having a  
25 degree of hydrolysis of from 80 to 95 mol% and a Höppler viscosity, in 4% strength aqueous solution, of from 1 to 30 mPa·s, are also preferred. Examples of these are partly hydrolyzed copolymers of vinyl acetate with hydrophobic comonomers, such as isopropenyl  
30 acetate, vinyl pivalate, vinyl ethylhexanoate, vinyl esters of saturated alpha-branched monocarboxylic acids having 5 or 9 to 11 carbon atoms, dialkyl maleates and dialkyl fumarates, such as diisopropyl maleate and diisopropyl fumarate, vinyl chloride, vinyl alkyl  
35 ethers, such as vinyl butyl ether, olefins, such as ethene and decene. The proportion of the hydrophobic units is preferably from 0.1 to 10% by weight, based on the total weight of the partly hydrolyzed polyvinyl alcohol. It is also possible to use mixtures of said

polyvinyl alcohols.

Further preferred polyvinyl alcohols are partly hydrolyzed polyvinyl alcohols which have been rendered hydrophobic and are obtained by polymer-analogous reaction, for example acetalation of the vinyl alcohol units with C<sub>1</sub>- to C<sub>4</sub>-aldehydes, such as butyraldehyde. The proportion of the hydrophobic units is preferably from 0.1 to 10% by weight, based on the total weight of the partly hydrolyzed polyvinyl acetate. The degree of hydrolysis of from 80 to 95 mol%, preferably from 85 to 94 mol%, and the Höppler viscosity (DIN 53015, method according to Höppler, 4% strength aqueous solution) is from 1 to 30 mPa·s, preferably from 2 to 25 mPa·s.

Most preferred are polyvinyl alcohols having a degree of hydrolysis of from 85 to 94 mol% and a Höppler viscosity, in 4% strength aqueous solution, of from 3 to 15 mPa·s (method according to Höppler at 20°C, DIN 53015). Said protective colloids are obtainable by means of processes known to the person skilled in the art.

Suitable starches are known to the person skilled in the art. The starch may originate from any desired sources. Examples are potato starch, corn starch, wheat starch, rice starch and tapioca starch. The starch may also be obtained from wastes, for example potato residues or potato peelings, or may be mixtures thereof. The starch may be used in natural form, as destructured starch, and as chemically modified starch, for example as hydroxyalkylated starch.

The polymers, in the form of their aqueous dispersions or their polymer powders, in particular their powders redispersible in water, are used in an amount of from 5 to 60% by weight, preferably from 5 to 25% by weight, in each case polymer weight based on the proportion of starch. Optionally, the starch compositions obtainable



thereby may also contain further additives, such as additional binders, for example those based on biodegradable polyesters, fillers, fibers of any type, in particular fibers of natural raw materials, such as  
5 cellulose (wood particles, woodmeal, wood fibers), straw or cotton, and pigments, lubricants and plasticizers, such as glycerols or sorbitols.

Particularly advantageous is the use of the polymers in  
10 starch compositions which, in addition to the starch and polymer, also contain cellulose fractions in the form of wood particles, wood fibers and woodmeal. Usually, the proportions by weight in this mixture are from 20 to 80% by weight of cellulose, from 10 to 50%  
15 by weight of starch and from 5 to 50% by weight of polymer, the proportions in each case summing to 100% by weight. These compositions are suitable for the production of wood extrudates, which are distinguished by their smooth surface.

20 For the preparation of the starch compositions, the proportion of starch and the polymer, and optionally further additives, are mixed with one another. The proportion of starch is preferably mixed in powder form  
25 with the pulverulent polymer, and optionally further additives are added. Starch compositions can be used as adhesives, preferably hotmelts, or can be further processed to give moldings.

30 Before the further processing to give moldings, the starch composition is optionally made into a paste with water. Preferably up to a proportion of water of from 10 to 40% by weight, based on the total mixture. With the use of polymer dispersions, this proportion of  
35 water can also be introduced via the polymer dispersion. The further processing can be effected using the tools customary for the processing of thermoplastics, by means of extrusion, extrusion blow molding, foam extrusion, injection molding, calendering

or thermoforming. In a preferred procedure, components are metered in premixed form or separately into the tool, for example an extruder, and are processed at temperatures of from 70°C to 150°C, preferably from  
5 80°C to 120°C.

In this way, rotable and nonrotable moldings, for example flowerpots and packaging materials, such as packaging fillers (foam extrudates) or films, are  
10 obtainable. Rotable is to be understood as meaning that the requirement of standard EN 13432 is fulfilled.

By the use according to the invention, shaped articles which have good mechanical strength, reduced water  
15 sensitivity, and little swelling in water and are rotable are obtainable. Particularly with the use of polymers in the form of their redispersion powders, a higher throughput and more stable and better bound pellets can be obtained on pelleting. The thermoplastic  
20 further processing of the pellets is promoted. The swelling in water is less, the strength and resilience are higher and, in the further processing (extrusion or injection molding), the addition of further thermoplastic polymers can be reduced or entirely  
25 omitted.

It is surprising that in particular the polymers containing crosslinkable N-methylol functions do not hinder the thermoplastic processing of the starch but  
30 even stabilize it. In the form of polymer powder, they are present as readily flowable and meterable powder which can be more readily and more rapidly incorporated and distributed in the thermomechanical process than polymer additives usually used, such as polyacetates or  
35 biopolyesters.

Examples:

The following materials were used:

Starch powder from potato residues having a residual moisture content of < 10% by weight.

Redispersed powder based on vinyl acetate/N-methylolacrylamide copolymer stabilized with a partly hydrolyzed polyvinyl alcohol.

Production of the test specimens:

10 The starch powder was made into a paste with 30% by weight of water, if appropriate after dry blending with the redispersion powder, and homogenized again in an RM100 Retsch mill for 10 min. The paste obtained was spread over Teflon-coated fabric framed by a 2 mm thick  
15 frame and then thermomechanically pressed with the existing residual moisture content in a press for 3 min at 120 bar pressure and 120°C plate temperature. In order to eliminate the resulting vapor pressure, 3 ventilation steps were carried out at 40 sec  
20 intervals. After cooling with water for 5 min, the press was opened and test specimens were cut from the sheets obtained and were left at room temperature until constant weight was reached (< 1% by weight residual moisture content).

25 The swelling behavior and dissolution on storage in water and the tensile strengths were investigated with these test specimens.

30 Determination of the swelling in water

In order to test the swelling in water, test specimens having an area of 2 x 2 cm<sup>2</sup> and a thickness of from 1.6 to 1.7 mm were used and were stored at 21°C in water,  
35 initially for 24 h. After the samples had been dried off with a cloth, the weight increase and increase in the thickness were measured immediately (24 h wet) and after storage in air for 24 h (24 h dry). Thereafter, the samples were placed again in water for a further

7 days and, after drying off, weight increase and increase in thickness were determined (7 d dry). After dry storage for 1 week, the remaining weight change and change in thickness were again measured (7 d dry).

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Table 1 summarizes the results, as mean values of 5 individual measurements. Test specimens of pure starch and with various added amounts of redispersion powder were investigated.

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Table 1:

Swelling in water of pressed sheets of starch with various added amounts of polymer

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Addition [% by wt.]	% weight change				% change of thickness			
	24 h wet	24 h dry	7 d wet	7 d dry	24 h wet	24 h dry	7 d wet	7 d dry
0	39.3	22.9	Disintegr.		17.7	5.5	Disintegr.	
6	41.7	-17.8	45.7	-46.8	20.8	-4.9	14.8	-73.0
10	40.1	-17.3	44.8	-34.6	17.6	-7	7	-69.4
15	34.5	-17.9	39.7	-38.7	8.4	-7.9	8.6	-68.3

The addition of polymer shows a significant improvement in the water resistance of the test specimens. In particular, disintegration on prolonged storage in water is prevented even with the addition of small amounts of 6% by weight of polymer. The short-term swelling (after 24 h) is dramatically reduced by additions of 15% by weight of polymer. The negative values after drying indicate a certain water-soluble fraction in the starch, which also cannot be bound in a water-resistant manner by the addition of polymer powder.

#### Tensile strengths

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For the tensile strength test, test strips 10 mm wide, 12 mm long and from 1.6 to 1.75 mm thick were used, and

tensile tests to fracture were carried out with a clamping length of 80 mm and a take-off speed of 5.0 mm/min under standard temperature and humidity conditions (50% relative humidity, 23°C).

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Table 2 summarizes the results (mean values of 6 individual measurements). Starch without addition and with various added amounts of redispersion powder was investigated:

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Table 2:

Tensile strengths of pressed sheets of starch/redispersion mixtures (two-component)

RD powder	Modulus of elasticity	Ultimate strength	Elongation	Breaking stress	Breaking length
% by wt.	N/mm <sup>2</sup>	N/mm <sup>2</sup>	%	N/mm <sup>2</sup>	mm
0	3400	5.09	0.195	3.74	0.178
6	3820	5.63	0.162	4.22	0.147
10	3220	7.02	0.373	5.11	0.369
15	3540	7.97	0.300	6.83	0.315

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While the modulus of elasticity scarcely changes, the maximum ultimate strength increases substantially with increasing addition of redispersion powder. The material remains hard and shows little elongation at maximum tensile force.

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The tests show that the strength of starch moldings can be substantially improved with additions up to 15%.

Pelleting tests:

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For the use of the material as a molding material in extrusion and injection molding, pelleting tests were carried out.

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The homogenization and pelleting to give granules were carried out in a 20 D twin-screw extruder at temperatures of from 80°C to 110°C. Pellets which

became strong and dust-free with addition of polymer were obtained.

The swelling of these pellets in water was investigated and a substantial reduction of the swelling in water and an improvement in the strength after storage in water were found.

The results of these investigations are summarized in table 3:

Table 3: Swelling of the pellets of starch/redispersion mixture in water

No.	Composition	Residual H <sub>2</sub> O [%]	H <sub>2</sub> O absorption [%]	Remark
1	Starch	5.6	177	Pellets have retained shape, have swelled to twice the size, from 3.89 mm to 5.04 mm, water yellow, pellets soft, spreadable
2	Starch + 15% of RD powder	5.8	132	Pellets have retained the shape, pellets have swelled to 0.5 times the size, water yellow, pellets somewhat harder

Tests with three-component material mixtures comprising starch, redispersion powder and thermoplastic polyester:

The following thermoplastic was incorporated into the materials already described above and comprising starch and redispersion powder, in order to obtain a readily thermoplastically processible mixture:

Linear polycaprolactone-polyester having an average molecular weight of 50 000, a melting point of 60°C and a melt flow rate (at 80°C, 44 psi) of 1.9 g/10 min.

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A mixture of (75-x)% by weight of starch, 25% by weight of polyester and x% by weight of redispersion powder was plasticated and homogenized on a mixing roll mill at a roll temperature of 130°C for 30 min (or in the presence of a redispersion powder for 5 min), and a roll hide having a thickness of 1 mm was produced.

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During processing, it was surprisingly possible to reduce the rolling time significantly from 30 min to 5 min by adding redispersion powder.

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This roll hide was placed in layers one on top of the other and pressed thermomechanically for 3 min at 120 bar pressure and 130°C plate temperature to give a material sheet having a thickness of 1.7 mm. Test strips 20.0 mm wide and 200 mm long were cut therefrom, and tensile tests were carried out with a clamped length of 100 mm and a take-off speed of 5.0 mm/min under standard temperature and humidity conditions (50% relative humidity, 23°C).

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The results are summarized as mean values of 6 individual measures in table 4:

Both the rupture force and the elongation increased considerably with increasing amount of RD powder. The RD powder improves not only the thermoplastic processibility but also the material properties obtained. The shaped articles are stronger, more resilient and more resistant to breaking.

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Table 4:

Tensile strengths of pressed sheets of three-component

mixtures of starch (75-x%), polyester (25%) and RD powder (x%)

RD powder	Modulus of elasticity	Rupture force	Elongation	Stress at rupture	Breaking length
x%	N/mm <sup>2</sup>	N/mm <sup>2</sup>	%	N/mm <sup>2</sup>	mm
0	21 700	41.7	0.318	41.2	0.615
4.5	21 400	72.7	0.571	70.4	1.050
7.5	23 100	117	1.270	115	2.280
11.25	23 000	102	1.190	102	2.210
37.5	22 600	129	1.300	129	2.560

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Test with three-component material mixtures comprising starch, redispersion powder and particulate woodmeal

10 parts by weight of the redispersion powder and  
 10 60 parts by weight of particulate wood, as obtained in wood processing by sawing and cutting and having a residual moisture content of about 10%, were to  
 20 parts by weight of corn starch, mixed with 2 parts by weight of linear PE wax as a lubricant and molded in  
 15 an extruder at temperatures of about 150°C and a pressure of about 200 bar to give pellets (3 mm).

The pellets were extruded in a conical twin-screw extruder at 150°C and a pressure of about 200 bar to give a shaped article.

20 The shaped article obtained had a uniform smooth surface which is readily processible similarly to a wood workpiece. The workpiece is very stable and has a flexural strength (according to ISO 868) of 31.5 N/mm<sup>2</sup> and a flexural modulus of elasticity of 3650 N/mm<sup>2</sup>. On  
 25 storage in water, it increases in weight by 11.6% after 1 hour.